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STATISTICAL STRUCTURE OF ANTHRONE

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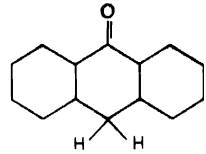
Plate II

ABSTRACT The space group of anthrone was found by Srivastava to be $P\,2_1/a$ with 2 molecules per unit cell This requires a molecular centre of symmetry. The chemical formula of anthrone molecule does not possess any centre of symmetry. In the rotation photographs of anthrone crystal about the symmetry axis, there occur diffuse blackenings midway between layer lines These are also corroborated by diffuse blackenings in appropriate positions in Weissenberg photographs. A statistical structure of anthrone crystal is proposed in order to explain these apparent anomalies

Anthrone belongs to space group $P2_1/a$ (Srivastava, 1957) with only two molecules per unit cell and having no symmetry centre in the structural formula



Theoretically, such a situation is untenable, but very long exposure such as 130 hrs. at 30KV, 25 mA failed to show any exception to the systematic absences on which the space-group determination was based. Moreover, there appeared diffused layer lines in between the regular layer lines when the crystal was rotated about the symmetry axis *b*, (Fig 1).

The position of these diffused layers were such as would have been occupied by the odd regular layer lines had the *b* axis been double A Weissenberg photograph for the same rotation axis in which the first of such diffuse layer is allowed through is given in Fig. 2. In this photograph the diffuse reflections are brought clearer.

One would naturally be tempted to assume a unit cell of double this size so that the unit cell may contain four molecules, which is also the necessary number of asymmetric units needed for this space group With the undoubled cell, the consecutive molecules along *b* axis should be identical as they are derived

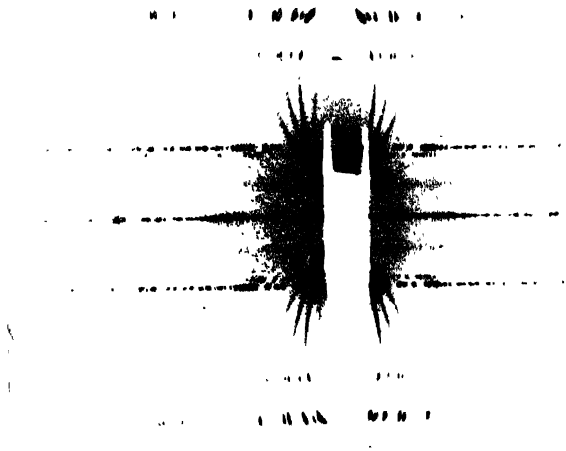


Fig. 1. Rotation about b-axis

Fig 2. Weissenberg photograph of the first diffuse layer line

by transl but in the doubled cell it is possible to assume the position of O interchanged with H H′ in the adjacent molecule With such picture can see that the contribution for *hkl* planes, where *k* is odd, can come only from the difference in the scattering powers of an oxygen atom and two hydrogen atoms attached to D and D′ respectively (Fig. 1).

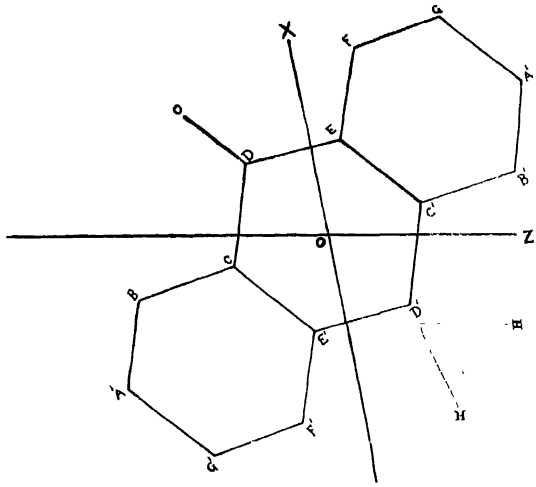


Fig 3 (The symbol O refers to the oxygen atom and all other letters refer to carbon atoms.)

One could imagine that due to some loose bonding occurring among the O and 2H of the consecutive anthrone molecules along the *b* axis their bonding with the carbon atoms to which they are attached might be weakened considerably, resulting in large thermal vibrations of this group of oxygen and hydrogen atoms. This should cause irregular ties in arrangements of those atoms This deviation from regular arrangement may be argued as reason for the appearance of diffuse layer lines for *k* odd values. But the diffuseness that is observed is of a much higher order than one would expect from thermal oscillations about certain mean positions. Further, diffuseness if caused in that way would also be found in spots on the regular layer lines, which is against observation The only possible structure that can explain the facts is that of random interchange between O and 2H atoms attached to the D and D′ carbon atoms. The structure is similar to that of anthraquinone with half of the oxygen atoms replaced by 2H atoms. The phenomenon is thus quite akin to that of order-disorder phenomenon in alloys. Thus each molecule of anthrone can now be considered

statistically to have half of oxygen and half of H, H′ attached to the D carbon atom and the other half to D′ for the purpose of calculating the structure factor for the sharp reflections. Consequently, the centre of symmetry that is necessary to be assumed to explain the X-ray diffraction spots is a statistical effect in which the oxygen and the hydrogen pair interchange positions in a random way keeping the statistical ratio the same.

The diffraction effect of such a structure can be visualised in the following way. The anthrone molecules less the oxygen and hydrogen atoms in the positions in question are arranged in the regular lattice corresponding to the space-group $P2_1/a$ and hence will give rise to diffraction maxima sharply only in the directions satisfying Laue equations corresponding to this space-group. An oxygen atom and a pair of hydrogen atoms are thus left over corresponding to each molecule. Had there been complete randomness these oxygen and hydrogen could give rise to some general scattering. The diffuse layers in between the regular layer lines show that there must be a preponderance of a periodicity double the axis length b. This can happen if the oxygen atoms as well as the hydrogen pairs have a tendency to face similar atoms rather than those of the opposite kind or that the anthrone crystal consists of a 1 : 1 combination of anthraquinone and 9, 10-dihydro-anthracene and occur at random throughout the structure while maintaining the basic lattice as given above and the proportion statistically with a considerable bias for the two types occurring in alternate layers. The first alternative is, however, improbable as it would mean that the attractions between the two oxygens and also of the two hydrogen pairs of the neighbouring molecules should be stronger than those between the oxygen of one molecule with the hydrogen pair of its neighbour. The second alternative, therefore, seems to be the correct solution. The intensity distributions in the diffuse layers are being studied with a view to knowing the domains of regularities and the nature of their distributions. The structure of 9, 10-dihydro-anthracene crystal is also under investigation as it is expected that it should have an isomorphous structure with anthraquinone, if our conclusions are correct.

REFERENCE

Srivastava, S. N., 1957, *Ind. J. Phys.*, **31**, 644.